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I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

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*Andrew Gersey*

Dated 26 January 2000

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24 DEC 1998

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PATENT 0.00 - 9828445.3

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
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1. Your reference PAI.50714/GB

2. Patent application number  
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9828445.8

3. Full name, address and postcode of the or of each applicant (underline all surnames)

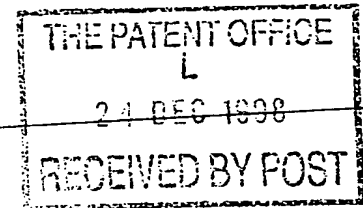
Imperial Chemical Industries PLC  
Imperial Chemical House  
Millbank  
London SW1P 3JF

Patents ADP number (if you know it)

6366090001

If the applicant is a corporate body, give the country/state of its incorporation

985003



4. Title of the invention

Coating Composition

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Steven Paul WARD

Patents & Trade Marks Section  
Legal Affairs Department  
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Coopers Building  
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0000158001

Patents ADP number (if you know it)

6626873001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

N/A

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
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N/A

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

# Patents Form 1/77

9. Enter the number of ☐ for any of the following items you ☐ with this form. Do not count copies of the same document

Continuation sheets of this form	No
Description	7
Claim(s)	2
Abstract	1
Drawing(s)	None

10. If you are also filing any of the following, state how many against each item.

Priority documents -

Translations of priority documents -

Statement of inventorship and right to grant of a patent (Patents Form 7/77) -

Request for preliminary examination and search (Patents Form 9/77) -

Request for substantive examination (Patents Form 10/77) -

Any other documents -  
(please specify)

11.

*S. Ward*

I/We request the grant of a patent on the basis of this application.

Signature

Steven Paul WARD

Date

Agent for the Applicant

23 December 1998

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr S P Ward  
01753 877123

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### Coating Composition

This invention relates to polyurethane coating compositions, their preparation and use.

Coatings used for the repair and refinishing of vehicles such as motorcars (known  
5 as vehicle refinish paints) are required to have very good physical properties such as  
hardness and resistance to water and solvents. The coating compositions are also required  
to have good application and appearance properties so that they are easy to apply to a  
substrate using spray application and result in final films having a good gloss.

One class of coating compositions commonly used for these applications  
10 comprises a hydroxyl functional polymer, such as a polyester or acrylic polymer, and a  
polyisocyanate. These two components react together after application to a substrate to  
form a polyurethane coating. These compositions are often thus referred to as  
'polyurethane coating compositions' although strictly the polyurethane is only formed  
when the coating crosslinks.

15 The two components of polyurethane coating compositions begin to react together  
as soon as they are mixed and for this reason these compositions are usually supplied in  
the form of two components which are mixed together shortly before use. Because of the

reaction between the components, the viscosity of the mixture begins to rise slowly right from first mixing. The mixed compositions have a limited useful life, referred to as the 'pot-life' after which the viscosity rise makes them unusable. Eventually, the mixed compositions in bulk become solid, or semi-solid. Typical pot-lives for vehicle refinish polyurethane coating compositions range from 30 minutes to 5 hours, typically 30 minutes to 3 hours.

Several different types of polyisocyanate are known for use in these types of composition, including the isocyanurate trimers of hexamethylene diisocyanate, and isophorone diisocyanate and polyisocyanate prepolymers made by reaction of these diisocyanates and others such as toluene diisocyanates with polyols such as trimethylol propane.

One other type of polyisocyanate is diphenylmethane diisocyanate, a mixture of 2 isomers, 4,4- and 2,4-, also known as MDI. MDI is widely used in producing polyurethane foams. MDI is available in several forms, based on two types of product, purified monomeric MDI and polymeric MDI. MDI is relatively cheap amongst polyisocyanates and polymeric MDI is a low viscosity liquid at room temperature. In these respects MDI would be ideal for use in polyurethane coating compositions for vehicle refinish paints, particularly for primers. However, the isocyanate groups on MDI are very reactive and it has been found impossible to simply use MDI as a direct replacement for the other useful polyisocyanates in these types of composition because the resulting compositions have too short a pot-life. Thus, it has not been realistically possible to use MDI in practical refinish paints even though it has several attractive properties.

We have now discovered that it is possible to formulate practical polyurethane coating compositions which contain MDI by using a particular hydroxyl containing component having secondary hydroxyl groups. This type of hydroxyl containing component has itself been suggested for use in polyurethane vehicle refinish paints but only in conjunction with a reactive diluent having blocked primary amine groups or hindered secondary amine groups which are ketimines, aldimines or aspartic esters. These reactive diluents are expensive and this is a disincentive to the use of these compositions. Furthermore these previously proposed compositions often have to be formulated as

three-pack compositions, the packs containing polymer, polyisocyanate and reactive diluent respectively, which makes them more complicated for the end-user to make up into the final paint. In contrast, the compositions of the present invention both avoid the use of expensive reactive diluents and utilise relatively low cost polyisocyanate to make  
 5 two-pack polyurethane compositions. These coating compositions have a good pot-life and which also give films having good properties. The compositions are particularly useful as primers for vehicle refinish.

According to the present invention there is provided a coating composition comprising ;

- 10 i) diphenylmethane diisocyanate, and
- ii) a hydroxyl functional compound which is a polyester having secondary hydroxyl groups,

the composition containing substantially no reactive diluent which are aldimines, ketimines or aspartic esters.

- 15 A further benefit of using diphenylmethane diisocyanate (MDI) is that the compositions do not require the presence of a reactive diluent to lower the viscosity of the composition, or to increase the speed of reaction of the components.

MDI is commercially available, for example as Suprasec MDI and MDI-based prepolymers from ICI Polyurethanes. MDI is preferably used in an amount such that  
 20 the ratio of isocyanate groups on the MDI to the total number of hydroxyl groups on the hydroxyl functional compound is in the range 0.7:1 to 3:1, more preferably 1:1 to 3:1.

Preferably the hydroxyl functional compound has a molecular weight of less than 5000, more preferably less than 2500 and most preferably less than 2000. Preferably the secondary hydroxyl groups on the hydroxyl functional compound are the product of a  
 25 reaction between a carboxylic acid group and an epoxide group.

Preferably the hydroxyl functional compound is the reaction product of a polyfunctional carboxylic acid and a monoepoxide, and so has secondary hydroxyl groups

arising from the reaction of the acid groups on the polycarboxylic acid with the epoxy group on the monoepoxide.

Preferred monoepoxides are glycidyl esters of C2-C20 alkanolic acids, preferably C8-C9 tertiary carboxylic acids such as versatic acid. One particularly suitable monoepoxide is Cardura E10<sup>TM</sup>.

The polyfunctional carboxylic acid can be a polyester with two or more carboxylic acid groups, preferably two to four carboxylic acid groups, more preferably two or three such groups. Polyesters are compounds containing more than one ester group. Acid functional polyesters can be made by conventional methods from a mixture of polyols, diacids and anhydrides. One preferred acid functional polyester can be made by reaction of a polyol with a carboxylic acid anhydride. Polyols are compounds with more than one hydroxyl group. Preferably the polyol has from two to six hydroxyl groups per molecule. Preferably the polyol has a molecular weight of 66 to 150. Examples of suitable polyols are ethylene glycol, propylene glycol, 1,4-butane diol, neopentyl glycol, hexane-1,6-diol, glycerol, trimethylol propane and pentaerythritol. Preferred anhydrides are cyclic internal anhydrides of dicarboxylic acids such as maleic anhydride, succinic anhydride, phthalic anhydride and hexahydroxyphthalic anhydride.

Preferably the reaction between the anhydride and the polyol is carried out substantially stoichiometrically so that one anhydride molecule reacts with each hydroxyl group on the polyol. The resulting polyfunctional acid compound has substantially the same number of acid groups as the polyol had hydroxyl groups. Because the hydroxyl/anhydride reaction occurs at a lower temperature than the carboxyl/hydroxyl or transesterification reactions, there are few side reactions and the molecular weight of the product can be controlled.

The reaction between the polyol and the anhydride can be carried out by dissolving the components in an organic solvent and then heating the solution preferably to between about 100 and 130°C for between about 1 and 3 hours so as to produce the polyfunctional carboxylic acid.



The reaction between the polyfunctional carboxylic acid and the monoepoxide can be carried out by adding the monoepoxide to a solution of the polycarboxylic acid in a suitable organic solvent in an amount so as to react each of the hydroxyl groups on the polyol with an epoxide group, and heating the mixture to between about 130 and 160°C for between about 2 and 12 hours.

The compositions can optionally contain a volatile organic solvent. The volatile organic solvent can be any solvent which will dissolve the polyisocyanate, and the hydroxyl functional compound. It can be an aliphatic or aromatic hydrocarbon such as Solvesso 100<sup>TM</sup>, toluene or xylene, an alcohol such as butanol or isopropanol, an ester such as butyl acetate or ethyl acetate, a ketone such as acetone, methyl isobutyl ketone or methyl ethyl ketone, an ether, an ether-alcohol or an ether-ester or a mixture of any of these.

Preferably the compositions contain less than 500 g/l of volatile organic solvent based on the total composition, more preferably less than 480 g/l still more preferably less than 420g/l and most preferably less than 250g/l.

The compositions can also contain catalysts for the isocyanate-hydroxyl reaction. Suitable catalysts include tin catalysts such as dibutyl tin dilaurate and amine catalysts such as triethylamine. The compositions can also contain other conventional paint additives such as, pigments, fillers, UV absorbers and flow aids. Preferably the composition is pigmented, that is, it also contains pigments and optionally fillers. Most preferably, the composition is pigmented so as to be useful as a vehicle refinish primer.

The compositions can be made by mixing the components, optionally dissolved in organic solvent, in any order.

The coating composition of the invention can be applied to the surface of a substrate and then allowed or caused to dry and cure. According to the present invention there is provided a process for coating a substrate which comprises the steps of applying a layer of a coating composition according to the present invention to a surface of the substrate and thereafter causing or allowing the layer to cure.

The coating composition can be applied by conventional means such as by brush, roller or spray, preferably spray. The substrate can be for example, metal, plastic, wood or glass. The compositions are particularly useful for refinishing motor vehicles, and especially as primers.

5        The applied layer can be allowed to cure at ambient temperature in the case where the hydroxyl polymer and crosslinker react together at ambient temperatures. Alternatively the layer can be baked at elevated temperatures, for example 50-120°C to accelerate curing. Drying and curing typically takes between 5 minutes and 24 hours depending on the ambient conditions and on the particular components used. Conveniently it takes about  
10 15 minutes to about 5 hours.

According to the present invention there is also provided a coated article obtainable by the process.

The invention will now be illustrated by means of the following examples.

### EXAMPLES

#### 15 Polyester 1

A mixture of neopentyl glycol (5.1 parts), 1,4-butanediol (4.5 parts) and hexahydroxy phthalic anhydride (30.4 parts) were heated under nitrogen to about 95°C so as to melt the components. The molten mixture was stirred and the temperature was slowly raised until an exotherm occurred at about 130°C. At this point, heating was stopped and the  
20 temperature went up to 170°C, then down to 150°C whereupon heating was resumed and the mixture was held at 150°C for 1 hour. The mixture was then allowed to cool for 1 hour. The mixture was heated back up to 150°C, Cardura E10™ (glycidyl ester of a C8-9 carboxylic acid from Shell, 50.0 parts) was added dropwise over a period of 3.5 hours and the mixture was allowed to cool to room temperature and left overnight. The mixture was  
25 heated to 150°C for a further 7 hours before being allowed to cool to room temperature. Butyl acetate (10 parts) was added to give a theoretical non-volatile solids content of 90%. The final measured acid value was 0.5 mgKOH/g based on non-volatile content. The number average molecular weight as measured by G.P.C. was 914.

### Primer composition

The following were added slowly in the order given to a mixture of Polyester 1 from above (27.8 parts), methyl isoamyl ketone (MIAK, 18.5 parts) and Byk 220S dispersant (2.78 parts), bentone (0.91 parts), talc (43 parts), extender (34.4 parts), titanium dioxide (43.3 parts), zinc phosphate pigment ZPA (18.2 parts), black tinter (2.3 parts) and defoamer (2.8 parts). The mixture was dispersed for a further 20 minutes. Further MIAK (6.0 parts) was added to form a pigmented primer base.

Polyester 1 (41.4 parts) and MDI (33.9 parts) were added to the primer composition and the mixture was thinned to 25 seconds BSB4 with MIAK.

- 10      The viscosity of the bulk composition was measured using a BSB4 cup 0.5 hours after making it as a guide to its pot-life to be 29 seconds.

Claims

1. A coating composition comprising;
  - i) diphenylmethane diisocyanate, and
  - ii) a hydroxyl functional compound which is a polyester having secondary  
5 hydroxyl groups,  
the composition containing substantially no reactive diluent which are aldimines,  
ketimines or aspartic esters.
2. A composition as claimed in Claim 1 in which the ratio of the isocyanate groups on  
the diphenylmethane diisocyanate to the total number of hydroxyl groups on the  
10 hydroxyl functional compound is 0.7:1 to 3:1.
3. A composition as claimed in claim 1 or claim 2 in which the hydroxyl functional  
compound has a molecular weight of less than 5000.
4. A composition as claimed in any one of claims 1 to 3 in which the secondary  
hydroxyl groups on the hydroxyl functional compound are the product of a reaction  
15 between a carboxylic acid group and an epoxide group.
5. A composition as claimed in any one of claims 1 to 4 in which the hydroxyl  
functional compound is the reaction product of a polyfunctional carboxylic acid  
and a monoepoxide.
6. A composition as claimed in Claim 5 in which the monoepoxide is a glycidyl ester  
20 of a C8-C9 tertiary carboxylic acid.
7. A composition as claimed in claim 5 or claim 6 in which the polyfunctional  
carboxylic acid is a polyester with two or more carboxylic acid groups.
8. A composition as claimed in any one of claims 5 to 7 in which the polyfunctional  
carboxylic acid is the reaction product of a polyol and an anhydride.
- 25 9. A composition as claimed in Claim 8 in which the polyol has from 2 to 4 hydroxyl  
groups.

- 10      A composition as claimed in any one of claims 1 to 9 which is pigmented.
11.      A process for preparing a composition as claimed in Claim 1 which comprises mixing
- i)      diphenylmethane diisocyanate, and
- 5          iii)     a hydroxyl functional compound which is a polyester having secondary hydroxyl groups,
- optionally dissolved in organic solvent.
12.      A process for coating a substrate which comprises the steps of applying a layer of a coating composition according to Claim 1 to a surface of the substrate and
- 10          thereafter causing or allowing the layer to cure.
13.      A coated substrate obtainable by the process of Claim 12.

ABSTRACTCoating Composition

A coating composition comprising ;

- i) diphenylmethane diisocyanate, and
- 5 ii) a hydroxyl functional compound which is a polyester having secondary hydroxyl groups,

the composition containing substantially no reactive diluent which are aldimines, ketimines or aspartic esters.

Sample 1. Plain cylindrical tube with an internal diameter of 25.4mm and a wall thickness of 2.29mm over braided with steel end fittings swaged at each end.

Sample 2. Smooth bore convoluted tube resulting from the processing of sample 1 in accordance with the methodology described with reference to the Fig. over braided with steel end fittings swaged at each end.

Test results

Sample 1      leakage rate 220 cc per hour.

Sample 2      leakage rate 150 cc per hour.

Since the weight of the tube per unit length in sample 2 was approximately 20% less than the weight of the material per unit length of sample 1, the figures were adjusted to give a figure for a tube of a given weight.

Thus the specific improvement in permeation resistance is

$$\frac{220}{150} \times \frac{5}{4} = 1.83$$

In other words, the specific permeation has been reduced in the ratio of 1:0.55.

Furthermore the flexibility is improved. In this regard sample 1 kinks at a bend radius of 381mm whereas sample 2 kinks at a bend radius of 63.5mm.

In a further test a comparison was made between a convoluted tube made by the method of the invention and one made entirely at a temperature below 327°C.

The results of the comparison are given below:

Sample 3 (Plain tube). Leakage Rate 241cc/h/m

Sample 4 (Convolute tube processed below 327°C ) Leakage rate 224cc/h/m.

Sample 5 (Convolute tube processed above 327°C and below 550°C and cooled below 327°C with a restraining force) Leakage Rate 148cc/hr/m.

Figures are permeation rates of helium at 29.6 At (30 Bar) at room temperature.

Below 327°C there is an apparent improvement of 7.6% whereas at above 327°C there is a very significant improvement of 62.8%.

In practice it has been found that best results are achieved when the temperature is between 327°C - 450°C, more preferably 327°C - 420°C , since deformation is achieved without straining the material beyond the elongation break limit in any position in the convolute configuration. The elongation limit increases with the processing temperature.

Whilst the invention has been specifically described with reference to a smooth bored convolute tube, it will be apparent to the skilled man that convolute tubes of various configurations can benefit from the method of the invention.



## CLAIMS

1. A method of producing a convoluted PTFE tube from a tube having an original wall thickness  $W_0$  comprising:
  1. subjecting the PTFE tube to a deformation force at a temperature at or above the gel transition temperature of PTFE to produce constrained convolutions and a thinned wall  $W_1$ ; and
  2. cooling the PTFE tube to below the gel transition temperature whilst continuing to constrain the deformations and thinned wall  $W_1$  until the convolutions become stable.
2. A method as claimed in claim 1 wherein the tube is placed on a mandrel and a helical tool comprising a leading end and a following end is rotated relative to the mandrel at a speed such that the leading end applies a deformation force at above the gel transition temperature and the following end applies a restraining force until the temperature has dropped below the gel transition temperature and the convolutions have become stable.
3. A convoluted PTFE tube comprising roots and peaks characterised in that it has an improved resistance to permeability and/or an increased tensile strength in the root of the convolutions compared to a non-convoluted tube having a wall thickness  $W_0$ .
4. A convoluted PTFE tube as claimed in claim 3 comprising a smooth bore and a convoluted outer wall.
5. A convoluted PTFE tube as claimed in claims 3 or 4 which on heating to above

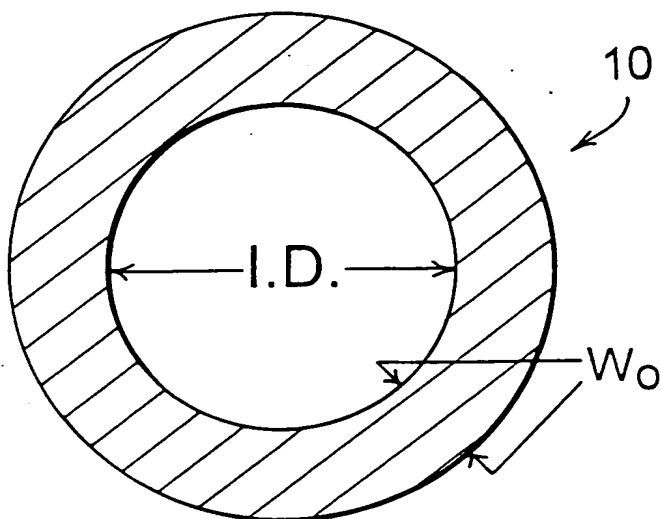
its gel transition temperature without a restraining force in place returns to within 20% of the tubes original wall thickness  $W_0$ .

ABSTRACTA PTFE TUBE

The present invention relates to a polytetrafluoroethylene (PTFE) tube and more particularly to a PTFE tube for a flexible hose. In particular the invention relates to a PTFE tube having a smooth bore for use in the production of a lined hose assembly further comprising hose braids, external hose protection and end fittings. It includes a method of producing a convoluted PTFE tube from a tube having an original wall thickness  $W_0$  comprising:

1. subjecting the PTFE tube to a deformation force at a temperature at or above the gel transition temperature of PTFE to produce constrained convolutions and a thinned wall  $W_1$ ; and
2. cooling the PTFE tube to below the gel transition temperature whilst continuing to constrain the deformations and thinned wall  $W_1$  until the convolutions become stable. The convoluted PTFE tube comprising roots and peaks characterised in that it has an improved resistance to permeability and/or an increased tensile strength in the root of the convolutions compared to a non-convoluted tube having a wall thickness  $W_0$ .

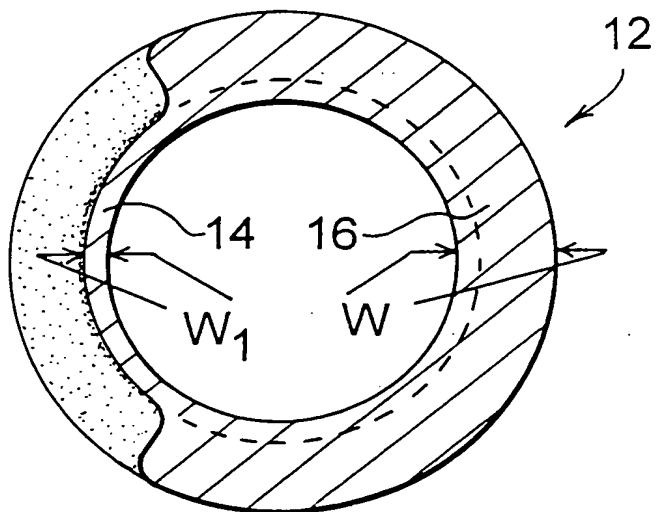
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(iii) heat above the gel transition temperature in the absence of a restraining force

(i) apply deformation force at or above the gel transition temperature

(ii) cool to below the gel transition temperature with a restraining force while convolutions become stable



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